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LAMINATED GLASS

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(56) Prior Art Documents
65038/80    C03C
GB 1576394
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(57) Claim

1.         A laminated pane including a glass sheet, a
transparent intermediate layer based on polyurethane
having energy-absorbing properties, and a transparent
coating layer of self-healing plastics material, notably
based on a thermosetting polyurethane, wherein said
intermediate layer based on polyurethane having energy-
absorbing properties is formed substantially of a
polyurethane obtained by reactive casting on a flat
horizontal support of a reaction mixture of an isocyanate
component of viscosity less than 5 Pas at $40^{\circ}C$ and a polyol
component, the isocyanate component including at least
one aliphatic or cycloaliphatic di-isocyanate or an iso-
cyanate prepolymer, the isocyanate component containing
urea functions, the content of urea being up to 10% of the
total weight of isocyanate component, the polyol
component including at least one long difunctional polyol
of molecular weight from 500 to 4000 and at least one

# COMPLETE SPECIFICATION

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Complete Specification for the invention entitled: "LAMINATED SAFETY PANE"

The following statement is a full description of this invention, including the best method of performing it known to me:—

good under very variable conditions of temperature and humidity, but the bio-mechanical properties of the pane and especially its resistance to shock are not entirely satisfactory.

5

There is also known from European Patent Publication 0054491 a laminated pane having the structure described above and in which the intermediate layer of plastics material having properties of absorption of energy is
10 based on a polyurethane polyurea having a linear structure and a content of urea groups of the order of 1 to 20% by weight, this polyurethane polyurea being the reaction product of a prepolymer obtained from a polyol component and an isocyanate component used in excess with at least
15 one diamine. This intermediate layer is made by extrusion of a polyurethane polyurea resin or by casting of a solution of said resin and evaporation of the solvents which in one case like the other requires a plurality of successive operations.

20

In the case of extrusion it is necessary to carry out a previous synthesis of the resin to be able to extrude it.

Further, to obtain the optical quality necessary for the
25 application envisaged it is necessary to "re-pass" the sheet. The optical quality obtained is not generally maintained with time as the plastics material retains in its memory its method of manufacture and the properties retained on "re-passage" are diminished with time.

30

Further, the extrusion of the layer having the properties of absorption of energy gives an assembly problem with the self-healing layer.

35 In the case of casting of a solution it is also necessary to carry out a previous synthesis of the resin. It is

+20°C from 250 to 500%, and a tear resistance Ra at
+20°C of at least 9 daN/mm.

In accordance with a further aspect of the present
invention there is provided a laminated pane including a
5  glass sheet, a transparent intermediate layer based on a
polyurethane having energy-absorbing properties, and a
transparent coating layer of self-healing plastics material,
notably based on a thermosetting polyurethane, wherein
the intermediate layer based on polyurethane having energy-
10  absorbing properties is formed substantially of a polyure-
thane obtained by reactive casting on a flat
horizontal support of a reaction mixture of an isocyanate
component having a viscosity less than 5 Pas at 40°C and
a polyol component, the isocyanate component including at
15  least one aliphatic or cycloaliphatic di-isocyanate or an
isocyanate prepolymer, the polyol component including at
least one long difunctional polyol of molecular weight
from 500 to 4000, at least one short diol as a chain
lengthening agent, and at least one polyol of functionality
20  greater than 2, the ratio of isocyanate group equivalents to
hydroxyl equivalents is about 1, the proportions of the
different polyols are chosen such that the number of hydroxyl
group equivalents due to the short diol represents from 20%
to 70% of the total of hydroxyl groups, this layer having
25  at a thickness of about 0.5 mm a flow stress $\sigma y$ at -20°C of
not more than 3 daN/mm$^2$, a rupture stress $\sigma_R$ at +20°C of at
least 2 daN/mm$^2$, a lengthening at rupture $\varepsilon R$ at +20° from
250 to 500% and a tear resistance Ra at +20°C of at least
9 daN/mm.

30  By reactive casting is meant casting in the form of a
layer or a film of a liquid mixture of the components in
the monomeric or prepolymer state, followed by polymerisation
of this

Suitable diisocyanates which may be used in the invention are chosen notably from the following aliphatic difunctional isocyanates: hexamethylenediisocyanate (HMDI), 2,2,4-trimethyl-1,6-hexanedii ...rnate (TMDI), bis 4-isocyanatocyclohexylmethane (Hylene W), bis 3-methyl-4-isocyanatocyclohexylmethane,2,2 bis(4-isocyanatocyclohexyl) propane,3-isocyanatomethyl-3,5,5 trimethylcyclohexyl-isocyanate (IPDI), m-xylylenediisocyanate (XDI), m- and p-tetramethylxylylenediisocyanate (m- and p-TMXDI),trans-cyclohexane-1,4 diisocyanate (CHDI), and 1,3 (diisocyanato-methyl)-cyclohexane (XDI hydrogenated).

IPDI is preferably used notably for reasons of cost.

According to one embodiment of the invention, there is used an isocyanate component containing urea functions. These urea functions improve certain mechanical properties of the layer. The content of urea may represent up to about 10% of the total weight of isocyanate component having urea functions. Preferably the content of urea is from between 5 and 7% of the total weight of said component. For the reason mentioned above there is preferably used 3-isocyanatomethyl-3,5,5 trimethylcyclohexylisocyanate comprising the urea functions (IPDI and derivatives).
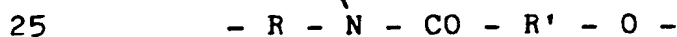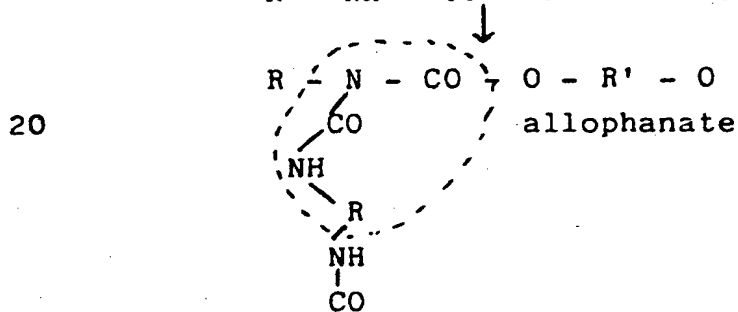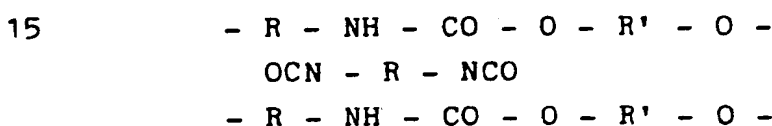
The long polyols which are suitable are chosen from polyetherdiols or polyesterdiols of molecular weight 500-4000; the polyesterdiols being products of esterification of a diacid such as adipic, succinic, palmitic, azelaic, sebacic, orthophthalic acid, and a diol such as ethyleneglycol, propanediol -1,3.butanediol - 1,4,hexanediol-1,6 and polyetherdiols of general formula
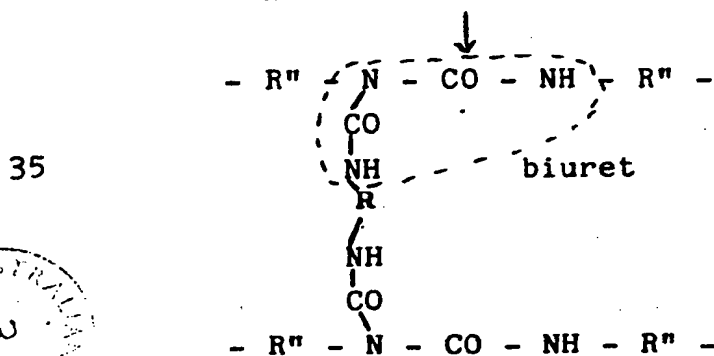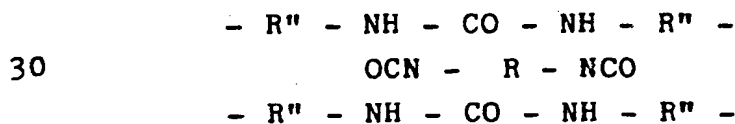
$$H \left\{ O (CH_2)_n \right\}_m OH$$
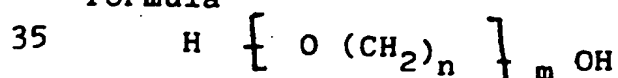
wherein n = 2 to 6; m is such that the molecular weight is from 500-4000, or the polyetherdiols of general formula

trifunctional components provides in surprising manner according to the invention in the case of starting components which are difunctional a layer which is not entirely thermoplastic when the ratio of NCO/OH groups is substantially equal to 1.

Reactive casting implies a rapid polymerisation reaction for the layer to be formed in a time compatible with industrial application. This requires a high temperature of the order of ~~about~~ 80 to 140°C, approximately, a temperature at which the secondary linking reactions are produced creating for example allophanate and/or biuret groups between the urethane chains such as:

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- R - NH - CO - O - R' - O -
  OCN - R - NCO
- R - NH - CO - O - R' - O -
                    ↓
  R - N - CO - O - R' - O
      CO            / allophanate
     NH
       R
     NH
     CO
- R - N - CO - R' - O -
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or

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- R" - NH - CO - NH - R" -
       OCN - R - NCO
- R" - NH - CO - NH - R" -
                ↓
- R"   N - CO - NH - R" -
       CO
       NH    biuret
       R
       NH
       CO
- R" - N - CO - NH - R" -
```

the polyol of functionality greater than 2 ~~about~~ $\overset{from}{}$ 0 to 0.35 equivalent. Under these conditions, the layer has the following mechanical characteristics measured according to standards AFNOR NFT 46.002, 51.034 and 54.108:

5

   - a stress at the start of flow $\sigma y$ at $-20^{\circ}$C not exceeding 3 daN/mm$^2$,
   - a stress at rupture $\sigma_R$ at $+20^{\circ}$C not less than 2 daN/mm$^2$,
10   - an elongation/$\overset{or\ lengthening}{}$ at rupture $\varepsilon_R$ at $+20^{\circ}$C from 250 to 500%,
   - resistance to start of tearing Ra at $+20^{\circ}$C greater than or equal to 9 daN/mm thickness.

15   According to another embodiment of the AE layer of the invention, the isocyanate component may contain limited proportions for example less than 15% of NCO equivalents of at least one triisocyanate such as a biuret of an isocyanate or a triisocyanurate.
20

According to one aspect of the invention, a part of the polyol component may be replaced by a product having different active hydrogens such as an amine.

25   An important advantage of the AE layer used according to the invention is that it may be formed by reactive casting on a first layer of plastics material which is already polymerised, thus finishing its polymerisation, notably the layer of self-healing plastics material without it
30   being necessary to treat the support layer.

The self-healing covering layer resistant to scratching of plastics material which is designated in this application as an interior protection layer (PI layer) is for example
35   described in French Patent Publications 2 187 719 and 2 251 608. This self-healing layer has under normal conditions of temperature a high capacity for elastic deformation, a small modulus in elasticity less than 2000

to 2000. Mixtures of different polyisocyanates and monomeric polyols may be used. A particularly preferred thermohardening polyurethane is that described in French Patent Publication 2 251 608.

5

The choice of thickness of the layer having properties of absorbtion of energy (AE layer) and that of the self-healing layer (PI layer) and the ratio between these two thicknesses are important factors. According to the
10   invention the total thickness of the two superposed layers is greater than 0.5mm with a thickness of at least 0.4mm for the layer having properties of absorbtion of energy.

Further, the adhesion between this layer and the sheet of
15   glass should be greater than about 2 daN/5cm, a value measured using a peeling test as described below. The force of adhesion should not however be too high, especially when there is used an AE layer of relatively small thickness close to the lower usable limit of about
20   0.4mm.

The layer having properties of absorption of energy may contain various additives which generally serve to facilitate its manufacture by reactive casting or which
25   may possibly, as the case requires, further improve certain of its properties.

It may contain a catalyst such as a tin catalyst for example dibutyltin dilaurate, tributyltin oxide. tin
30   octoate, or an organomercuric catalyst for example mercury phenyl ester, or an amine catalyst, for example diazabicyclo(2,2,2)-octane, or 1,8 diazabicyclo (5,4,0)-1 decene-7.

35   The layer may contain a stabiliser such as bis (2,2,6,6-tetramethyl-4 piperidyl) sebacate, or a phenolic antioxidant.

Examples of manufacture of laminated panes according to the invention are described in the following.

## Example 1

On a moving glass support passing in continuous manner, coated with a separation agent which may, for example, be that described in French Patent Publication 2 383 000, that is to say a modified addition product of ethylene oxide, there is cast a homogeneous mixture with the following proportions of:

- 1000 g of a polyether of molecular weight of ~~about~~ 450 obtained by condensation of 1,2-propylene oxide with 2,2-bis (hydroxymethyl)- 1-butanol and having a content of hydroxy free radicals of about 10.5 to 12% containing 1% by weight of stabiliser, 0.05% by weight of a catalyst, that is dibutyltin dilaurate and 0.1% by weight of a spreading agent.

- 1020 g of a biuret of 1,6-hexanediisocyanate having a content of free isocyanate radicals of about 23.2%.

There is used a casting head such as that described in French Patent Publication 2 347 170. There is formed a uniform layer which after polymerisation under the effect of heat, for example about 15 minutes at 120°C, has a thickness of about 0.19mm and self-healing properties.

To make the layer having properties of absorption of energy there is first prepared the polyol component by mixing a polytetramethyleneglycol of molecular weight 1000 (for example the product sold commercially under the name Polymeg 1000 by the QUAKER OATS Company), with 1,4-butanediol, the proportions of the two constituents being such that the polytetramethyleneglycol supplies 0.37 equivalents in hydroxyl groups whereas the butanediol-1,4 gives 0.63.

described in European Patent Publication 0 015 209, the AE layer being applied against the internal surface of the glass and a second stage consisting of disposing the laminated product obtained in an autoclave, where, for about an hour it is subjected to a pressure of about 10 bars at a temperature of about 135°C. This autoclave cycle may possibly be replaced by a stoving cycle without increased pressure.

The pane obtained has excellent optical quality and perfect transparency.

The adhesion obtained between the glass sheet and the layer having the properties of absorption of energy is measured for the manufactured pane by a peeling test described below.

There is cut a strip of 5cm width from the covering sheet having two layers. An end of the strip is unstuck and there is applied thereto a pulling force perpendicular to the surface of the glass with a pulling speed of 5cm per minute. The operation is carried out at 20°C. The force of traction necessary for unsticking of the strip is noted. Operating thus there is obtained a traction force of 10 daN/5cm.

Trials for resistance to shock at different temperatures are carried out on the pane made according to this example.

The first trial for resistance to shock is carried out with a steel ball of weight 2.260kg (heavy ball test) which is caused to fall on the central part of a square sample of laminated glass of 30.5cm side, held on a rigid frame. There is determined the approximate height from which 90% of the samples tested at the chosen temperature resist fall of the ball without the ball passing through.

The peeling test provides a value of 8 daN/5 cm.

These values are insufficient which shows that the reactive casting used in Example 1 gives the AE layer the desired properties.

Example 2
The procedure of Example 1 is carried out except that there are made layers with different thicknesses, that is a self-healing layer (P I) of 0.41mm thickness and an AE layer of 0.29 mm thickness.

The laminated pane obtained has the following characteristics:

The peeling test gives a value of 10 daN/5cm. The heavy ball test and the two tests with a light ball give respective values of 3.5, 9 and 9 metres which is insufficient. These poor values are due to the insufficient thickness of the layer having properties of absorption of energy.

Example 3
The procedure of Example 1 is followed, except that there is made a P I layer of 0.315 mm thickness and an AE layer of 0.415mm thickness.

The peeling test gives the value of 10 daN/5cm. The tests with the heavy ball and the light ball give respective values of 4.5, 10 and 13 metres which is satisfactory.

Example 4
The procedure of Example 1 is carried out except that there is made a PI layer of 0.32mm thickness, an AE layer of 0.42mm thickness and the surface of the glass before assembly is subjected to a known treatment with an adhesion promoter such as a silane to obtain a higher value of adhesion.

There are made layers of 0.160mm thickness for the PI layer and 0.660mm thickness for the AE layer.

The pane obtained has optical and mechanical characteristics which are completely satisfactory. The values measured for different tests are as follows: an adhesion of 3 daN/5cm, and values of ball tests of 9, 13 and 13 metres.

Example 7

The procedure of Example 6 is followed except that the proportions of different polyols are respectively 0.35 OH equivalents for the Polymeg 1000, 0.45 OH equivalents for the 1,4-butanediol and 0.20 OH equivalents for the Niax 301.

There are made layers of 0.31mm thickness for the PI layer and 0.48mm thickness for the AE layer.

The values measured in tests are as follows: an adhesion of 3 daN/5cm, values of 4.5, 10 and 12 metres for balls, which is satisfactory.

Example 8

The procedure of Example 7 is followed except that there are used thicknesses of 0.39mm for the PI layer and 0.39mm for the AE layer.

The values measured are as follows: an adhesion of 4, values of 3, 8 and 8 for the balls, which is insufficient.

This example compared with Example 7 shows that for a same thickness for the sheet having two layers there exists a ratio of thickness between the AE layer and the PI layer which, according to the value, gives a pane which may or may not be satisfactory.

The claims defining the invention are as follows:

1.        A laminated pane including a glass sheet, a
transparent intermediate layer based on polyurethane
having energy-absorbing properties, and a transparent
coating layer of self-healing plastics material, notably
based on a thermosetting polyurethane, wherein said
intermediate layer based on polyurethane having energy-
absorbing properties is formed substantially of a
polyurethane obtained by reactive casting on a flat
horizontal support of a reaction mixture of an isocyanate
component of viscosity less than 5 Pas at $40^{\circ}C$ and a polyol
component, the isocyanate component including at least
one aliphatic or cycloaliphatic di-isocyanate or an iso-
cyanate prepolymer, the isocyanate component containing
urea functions, the content of urea being up to 10% of the
total weight of isocyanate component, the polyol
component including at least one long difunctional polyol
of molecular weight from 500 to 4000 and at least one
short diol as a chain lengthening agent, the ratio of
isocyanate group equivalents to hydroxyl group equivalents
is about 1, the proportions of the different polyols are
selected such that the number of hydroxyl group equivalents
due to the short polyol represents from 20 to 70% of the
total hydroxyl groups, and this layer having at a thickness
of about 0.5 mm, a flow stress $\sigma y$ at $-20^{\circ}C$ not exceeding
3 $daN/mm^2$, a rupture stress $\sigma_R$ at $+20^{\circ}C$ of at least 2
$daN/mm^2$, a lengthening at rupture $\varepsilon R$ at $+20^{\circ}C$ from 250
to 500%, and a tear resistance Ra at $+20^{\circ}C$ of at least
9 daN/mm.

2.        The laminated pane as claimed in Claim 1,
wherein the content of urea is from 5% to 7% of the total
weight of said isocyanate component.

6.          The laminated pane according to any one of
Claims 3 to 5, wherein the polyol of functionality
greater than 2 is a triol.

7.          The laminated pane according to any one of
Claims 3 to 6, wherein for one hydroxyl equivalent in
total f   ne polyol component of the polyurethane having
energy-absorbing properties, the long polyol represents
from 0.30 to 0.45 equivalent, the short diol from 0.2 to
0.7 equivalent and the polyol of functionality greater
than from 2.0 to 0.35 equivalent.

8.          The laminated pane according to any one of
Claims 1 to 7, wherein the polyurethane layer having energy-
absorbing properties includes additives, such as a catalyst,
a spreading agent and a stabiliser.

9.          The laminated pane according to any one of
Claims 1 to 8, wherein the thickness of the polyurethane
layer having energy-absorbing properties increased by the
thickness of the coating layer is greater than 0.5 mm, with
a thickness of at least 0.4 mm for the layer having energy-
absorbing properties.

10.          The laminated pane according to any one of
Claims 1 to 9, wherein the adhesion between the layer
having energy-absorption properties and the glass sheet
is greater than 2 daN/5 cm.

11.          The laminated pane according to any one of
Claims 1 to 10, wherein the polyurethane layer having
energy-absorbing properties is obtained by polymerisation
at a polymerisation temperature which is from $80^{\circ}C$ to
$140^{\circ}C$ during reactive casting.

12.          The laminated pane according to any one of
Claims 1 to 11, wherein the isocyanate component further
comprises at least one tri-isocyanate.